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PATENT
Customer No. 22,852
Attorney Docket No. 07648.0002-00000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Jian Li et al.

Application No.: 09/513,207

Filed: February 24, 2000

For: SIMULTANEOUS AND RAPID
DETERMINATION OF MULTIPLE
COMPONENT
CONCENTRATIONS IN A MULTI-
COMPONENT CHEMICAL
PROCESS STREAM

)
)
) Group Art Unit: 1743

)
) Examiner: A. Soderquist

)
)
) Confirmation No.: 6210

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION UNDER 37 C.F.R. § 1.131

I, Xin-Sheng CHAI, state that I am one of the named applicants of the above-identified application and am one of the co-inventors of the subject matter described and claimed therein. On or before April 1, 1999, we completed in this country the invention as described and claimed in the above-identified application as evidenced by experiments discussed in the attached Invention Disclosure (Exhibit A).

The Invention Disclosure indicates that the claimed invention was reduced to practice before the publication date of the article by Walter M. Doyle and Lani Tran entitled "Analysis of Strongly Absorbing Chromophores by UV/Visible ATR Spectroscopy" in *Spectroscopy*, volume 14, number 4 (April 1999). Doyle discusses the

DECLARATION UNDER 37 C.F.R. § 1.131
Application Serial No. 09/513,207
Attorney Docket No. 07648,0002-00000

attenuated total reflectance (ATR) sampling technique for analysis in the UV/Visible light spectrum and discloses a tunnel flow cell configuration for measuring the UV/Visible absorption of different liquids. The reference does not, however, disclose use of an ATR technique to sample the UV/Visible spectrum of a liquid kraft liquor stream.

The Invention Disclosure provides descriptions of experimental examples on alkali, carbonate, and sulfide concentration tests on kraft liquors made using ATR-UV spectroscopy that were conducted prior to the publication of the Doyle article. Specifically, these experiments used both methods and systems described in the application for simultaneously determining multiple individual chemical concentrations of a liquid kraft liquor stream using multivariate regression methods and an ATR device to sample the UV absorbance spectrum of the liquid from 190 to 300 nm. Thus, as evidenced by the descriptions of the methods and systems used and results of the experimental examples provided in the Invention Disclosure, the present invention was reduced to practice before the publication date of the Doyle article.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that the statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patents issuing thereon.

Dated: June 23, 2004

By: 

Xin-Sheng CHAI



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)	
)	
Jian Li et al.)	Group Art Unit: 1743
)	
Application No.: 09/513,207)	Examiner: A. Soderquist
)	
Filed: February 24, 2000)	
)	
For: SIMULTANEOUS AND RAPID)	Confirmation No.: 6210
DETERMINATION OF MULTIPLE)	
COMPONENT)	ATTENTION: OFFICE OF PETITIONS
CONCENTRATIONS IN A MULTI-)	
COMPONENT CHEMICAL)	
PROCESS STREAM)	

EXHIBIT A

Invention Disclosure

W2

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

INVENTION DISCLOSURE

INSTRUCTIONS:

- Please complete an original and one copy of this form.
- Sign and date every page in ink, and have each additional sheet initialed by at least one corroborator who fully understands the disclosure.
- All attachments, including sketches and drawings, must be signed and corroborated. Every question must be answered completely. If "none" applies, so state. Use additional sheets when necessary.
- If the disclosure is to be patented, attach a preliminary patent search of similar patents from PAPERCHEM through IPST's Information Services Division. Include a copy of the search with relevant comments by the inventor regarding similarities.
- Retain the copy of the disclosure for your records, and forward the original to the office of the Vice President-Administration, room 522.

TITLE OF THE INVENTION: Simultaneous and Rapid Determination of Effective Alkali, Carbonate, and Sulfide in Kraft Liquors

DESCRIPTION:

Enter here the number of additional sheets attached to the 3 disclosure pages, if any _____
(Do not include pages of PAPERCHEM search.)

Inventor (1) Jian Li
(Typed Name)

Xinsheng
Inventor (2) Junyong
(Typed Name)

Signed: [Signature]
Date: REDACTED
Month Day Year

Signed: [Signature]
Date: REDACTED
Month Day Year

IS THIS INVENTION ASSOCIATED WITH A FEDERALLY-FUNDED PROJECT? ☒

If yes, which project (name and number)? 415701 - VOC control in Kraft Mills

Name/address of federal contract coordinator to be notified that disclosure is being filed:

Gordon R. McClellan, Project Officer and
Contracting Officer's Representative (COR)
U.S. Department of Energy
Idaho Operations Office
Laboratory Development
850 Energy Drive/Mail Stop 1150
Idaho Falls, Idaho 83401-1562

CORROBORATION

The foregoing signed disclosure was explained to me, and understood by me, on the date set forth below.

Corroborator (1) Charles E. Couruhene
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Corroborator (2) MARY TURNER
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Signed: Mary Turner

Date: **REDACTED**

Month Day Year

INVENTION DISCLOSURE:

1. The idea was first conceived on

REDACTED

2. This idea was first disclosed to others on

REDACTED

3. The person(s) to whom this idea was first disclosed:

Mike Doyle, Axiom Analytic Inc.

4. The manner in which this idea was first disclosed was:

Liquor sample testing by the ATR cell manufacturer, Axiom.

5. The first written description of this idea is in the form of

This disclosure.

6. The first sketch or drawing of this idea in the form of

Drawing

was/will be made

now located

4684

(laboratory note book #)

7. The first act(s) other than making a drawing or a written description or making a verbal disclosure which if proven, would establish conception of the invention was/were

Sample

Liquor test by Axiom

8. The first structure embodying this idea in the form of

This disclosure

was/will be made

and located at

INVENTION DISCLOSURE
(continued)

REDACTED

9. This idea was/will be first actually tried out

10. This idea was/will be first put in use for a purpose other than to try it out to see if it works on

_____ ; Where _____

11. This idea was/will be offered for sale on _____

Where _____ How _____

Inventor (1) Jian Li
Typed Name

Xin-Sheng Chai

Junyong Zhu

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Atlanta, GA, 30318

Signed: _____

Date: _____

REDACTED

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Typed Name

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Signed: Chai, Xin

Date: _____

Month

Day

Year

REDACTED

I request this disclosure be processed as indicated:

_____ Held in a disclosure file for the present.

_____ Request patent attorney perform a preliminary search for patentability.

_____ Request patent attorney perform proceed immediately with patenting process.

Reviewed by Patent Counsel
Signed: W. Malcolm
IPST Division Director

STATE OF GEORGIA)
)
COUNTY OF FULTON)

SS:

I hereby certify that before me at the Institute of Paper Science and Technology in Atlanta in the County of Fulton and State of Georgia, personally appeared _____, personally known by me, who then and there acknowledged that the foregoing assignment was duly signed, sealed, and delivered by him on the date appearing at the foot thereof.

_____, 1996

Notary Public

My Commission Expires: _____

Simultaneous and Rapid Determination of Effective Alkali, Carbonate and Sulfide Concentrations in Kraft Liquors

Jian Li, Xin-Sheng Chai, Junyong Zhu
Institute of Paper Science and Technology
500 10th Street, NW, Atlanta, GA, USA, 30318

ABSTRACT

A new rapid method provides the on-line and simultaneous determination of effective alkali, carbonate and sulfide concentrations in kraft liquors used for kraft pulp production. This method can be used to control white liquor causticizing efficiency, sulfate reduction efficiency in green liquor, and oxidation efficiency for oxidized white liquor, as well as the active and effective alkali charge to kraft pulping operation. This method can be used as an on-line device (i.e. a small liquor stream cycling through the device from main liquor line or container) or in-line device (i.e. a probe inserted into the targeting liquor line or container). Thus, it eliminates manual sampling, and does not require liquor dilution. The cost of instrumentation, i.e. ATR-UV, used in this method is much less than that used in other methods, e.g. Near-IR and ATR-FTIR. The device does not need frequent maintenance. The determination is obtained by passing a targeting liquor stream through an ATR (attenuated total reflectance) flow cell installed in an UV spectrometer, measuring the ATR-UV absorbance spectrum of the liquor over a predetermined range of wave length, and calculating the component concentrations with the obtained spectrum and the multivariate calibration program. This multivariate calibration program uses a calibration file built from the spectra of many standard liquors with known, but different combinations, concentrations of sodium hydroxide, sodium sulfide, sodium carbonate, sodium chloride, sodium sulfate and sodium thiosulfate.

BACKGROUND OF THE INVENTION

i) Field of the invention

This invention relates to a method for determining major chemical concentrations in aqueous liquors used in cellulosic pulp manufacturing processes. More specifically this invention relates to an on-line and/or in-line method of determining sodium hydroxide, sodium sulfide, and sodium carbonate concentrations in kraft liquors, such as white liquor, green liquor, and oxidized white liquor. The invention relates to the application of Attenuated Total Reflectance – Ultraviolet spectroscopy for measurement of the absorbance of these kraft liquors.

ii) Description of prior art

In kraft pulping, lignocellulosic material, e.g. wood chips, is treated with white liquor containing active pulping chemicals, i.e. sodium hydroxide and sodium sulfide (the sum of the sodium hydroxide and one half of the sodium sulfide is known as effective alkali). Cellulosic fibers are released from each other when lignin is dissolved in the liquor under elevated temperature. The concentrated spent pulping liquor, black liquor, is burned in a chemical recovery furnace, where sulfur compounds are reduced to sodium sulfide. A green liquor is formed when the smelt of inorganic ash is dissolved in water, containing mostly sodium sulfide and sodium carbonate. The sodium carbonate is converted to sodium hydroxide in the recausticizing plant by reacting with calcium hydroxide in water. By then, the active pulping liquor is regenerated.

Kraft delignification rate and selectivity are strongly affected by the white liquor quality, i.e. NaOH and Na₂S concentrations. The goal of kraft recovery is to produce white liquor with high concentration of NaOH and Na₂S, and low in Na₂CO₃ and Na₂SO₄. This goal requires accurate and in-situ measurement of white and green liquor compositions to allow operator or control system make timely adjustment of process conditions.

Current on-line sensors developed for white liquor analysis are based on conductivity, FTIR, NIR or conventional UV spectroscopy. However, sensors based conductivity, FTIR and conventional UV can only provide a single component measurement, e.g. conductivity and FTIR give EA concentration, and conventional UV gives only sulfide concentration. A recent technique based on NIR (US patent 5,616,214) may be able to measure simultaneously the concentrations of these components. However, the cost of NIR and FTIR instrument is quite higher than UV based instrument. The conventional UV requires very high dilution, above 10,000, of the process liquor before the analysis.

Therefore, on-line or in-line sensors are needed for the measurement of white, green and oxidized white liquor compositions. They should be **rugged, low cost, easy to install and operate**, and provide **simultaneous output** of **several** concentrations or measurement values from a **single** sensor.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a method for simultaneously determining effective alkali, carbonate and sulfide concentrations in kraft liquors used for kraft pulp manufacturing processes. The device used in this method is **rugged, low cost, easy to install and operate**, and provide **rapid and simultaneous output** of **several** concentrations or measurement values from **single** measurement.

This method can be used as an on-line device (i.e. a small liquor stream cycling through the device from main liquor line or container) or in-line device (i.e. a probe inserted into the targeting liquor line or container).

It eliminates manual sampling, and does not require liquor dilution. The device does not need frequent maintenance.

The determination is obtained by passing a targeting liquor stream through an ATR (attenuated total reflectance) flow cell installed in an UV spectrometer, measuring the ATR-

UV absorbance spectrum of the liquor over a predetermined range of wave length, and calculating the component concentrations with the obtained spectrum and the multivariate calibration program. This multivariate calibration program uses a calibration file built from the spectra of many standard liquors with known, but different combinations, concentrations of sodium hydroxide, sodium sulfide, sodium carbonate, sodium chloride, sodium sulfate and sodium thiosulfate.

DETAILED DESCRIPTION OF THE INVENTION

Sensor Setup and Procedure

The method of this simultaneously determine effective alkali, carbonate and sulfide concentrations in kraft liquors used for kraft pulp manufacturing processes.

The concentrations determined by this method determine causticizing efficiency from green liquor to white liquor, sulfate reduction efficiency in chemical recovery furnace, and oxidation efficiency of white liquor oxidation reaction. Also these concentrations determines the accurate active and effective alkali charge to kraft pulping operation.

This method can be used as an on-line device (i.e. a small liquor stream cycling through the device from main liquor line or container) or in-line device (i.e. a probe inserted into the targeting liquor line or container).

In the case of on-line determination, a targeting liquor stream is withdrawn from a liquor storage tank, a reactor, or a transport line by a pump. The small liquor stream (~10 to 100 cc/min) is preferably filtered to move solid particles, and then sent through an ATR (attenuated total reflectance) Tunnel flow cell. This ATR cell is installed in an UV spectrophotometer. Figure 1 shows the device setup. The ATR-UV absorbance spectrum of the liquor sample over a predetermined range of wavelength, i.e. 190 to 300 nm, is scanned within 2 seconds, and recorded by a computer. The spectrum is then analyzed by the multivariate calibration program in the computer, and the concentration of each individual chemical is computed.

In the case of in-line determination, an ATR optical probe is inserted into the targeting liquor tank, reactor, or liquor transporting line. The ATR-UV absorbance spectra are then transferred to an UV spectrophotometer via optical fibers. The remaining data analysis of the spectrum is the same as that for on-line determination. Figure 2 shows the device setup.

ATR-UV Spectroscopy – Principle of the Invention

The method of the invention is based on the modern ATR-UV technology. ATR-UV technology eliminates the high dilution problem (up to a dilution factor of 50,000) in conventional UV spectroscopy for industrial process analysis. Further more, it can provide multi-component measurements through computer analysis of the complex UV spectrum. The measuring principle of the ATR-probe is demonstrated in Figure 3.

In ATR spectroscopy a transparent probe of high refractive index (n_p) is brought into contact with a sample which must have a lower refractive index (n_s). Light from a spectrometer is lead to the probe via optical fibres and collimated before being introduced into the probe at an angle θ towards the boundary surface. If the angle of incidence, θ , is greater than the critical angle θ_c ($\sin \theta_c = n_s / n_p$), total reflection will occur when the beam of light hits the boundary. In each reflection at the boundary between probe material and sample, the light penetrates a short distance into the outer medium (sample) in the form of an evanescent wave [1, 2]. During this short transection, light can be absorbed by the sample so that the transmitted beam carries information about its spectral properties. The

light leaves the probe through a lens focusing it onto a fiber that will bring the light back to the spectrometer for measurement. The optical path length is roughly 1-2 μm per reflection. Therefore, it can be used for measuring very concentrated absorbed species in the solution without diluting the sample.

In addition to the extremely short optical path length, there is a very important and unique feature of the ATR-UV spectrum, which is very different from conventional UV spectrum and makes it being more powerful than conventional UV technique. The actual or effective pathlength, b_{act} , is not a constant parameter for a given ATR flow cell or probe. It is a function of the wavelength, refractive indices n_s and n_p , and angle of incidence. Thus, the absorption of a chemical at a fixed concentration, and a given wavelength can vary differently if other components have an effect on the solution refractive index n_s even they do not adsorb UV light at that wavelength. Since different chemical compounds contribute to solution refractive index differently, the resulting ART-UV spectrum, thus, contains the large amount of information about a given solution. This ART-UV spectrum will provide the component concentrations when it is analyzed by the multivariate regression method.

In conclusion, the extremely short and variable path length makes this invention possible.

Multivariate Regression Calibration Using Partial Least Squares (PLS) Method

Quantitative analysis is based on a relationship between the detector response of the instrument and the concentration of the interested component in the sample. The idea of the partial least squares PLS method of calibration is to reconstruct the spectrum of a mixture by adding fractions of pure component spectra and predict the concentrations of the interested components in the unknown sample. By using some mathematical manipulations and regression techniques, a number of independent mathematical pure component spectra (called the loading vectors B) are created from the spectra of the large calibration set. The fractions by which the loading vectors are weighted (called the scores T) to reconstruct the spectra of the mixtures are also calculated in the calibration algorithm. The matrix notation of the PLS method is $A(n,m) = B(n,h)T(h,m) + E(n,m)$, where h , m , n are the number of loading vectors, sample spectra and chosen wavelengths respectively. Once the calibration coefficient matrix is created, the concentrations of the components in an unknown sample can be determined by reconstructing the unknown spectrum from the loading vectors in the calibration set. The PLS method combines the advantages of *classical least squares* (CLS) and (*inverse least squares*) ILS since a large number of standards can be used for determination using multiple wavelengths from the whole spectra. Furthermore, effect such as temperature, baseline shifts and component interactions in the sample can be included in the loading vectors and the scores. The method is very suitable for quantitative determination from complicated unknown spectra such as ATR-UV spectroscopic determination of pulping liquors.

With this mathematical tool, a multivariate calibration is built from the spectra of many standard liquors with known, but different combinations, concentrations of sodium hydroxide, sodium sulfide, sodium carbonate, sodium chloride, sodium sulfate and sodium thiosulfate.

ATR-UV Spectra of Some Chemical Solutions for Kraft Liquors

Figure 4 shows the three ATR-UV spectra of concentrated solutions for pure sodium hydroxide, carbonate and sulfide. Sulfide solution shows strong absorbance at wavelength range of 190 to 260 nm. Sodium hydroxide and carbonate have slightly different absorbances at wavelength around 200 nm.

As it was discussed in earlier section, the absorbance in ATR-UV technology change differently from the conventional UV because of the variable path length. Thus, it does not follow the linear Beer's Law as they are demonstrated by Figures 5, 6, and 7.

Figure 8 shows solutions of effective alkali, sulfide and carbonate. The concentration of each component was changed randomly.

EXAMPLES

1.

With chemometrical, i.e. the PLS, method, a good calibration file used for predict the concentration of these components can be built up. Table 1 shows the data of training set for the calibration model, which is over the whole possible range for the concentrations of effective alkali, sulfide and carbonate in white and green liquors. Figures 9, 10, and 11 show the calibration graphs for EA, sulfide and carbonate, respectively. The linear relationships shown indicate that such calibration model can be built. The agreement between the observed and predicted for EA and sulfide is very well. The agreement for carbonate at low concentration, i.e. 0.12 M, is not very good, which, however, is not very important for kraft pulp mill. Since causticizing efficiency normally never gets beyond 90%, the carbonate concentration in all kraft liquors should normally be above 0.3 M. In addition, such error can be further reduced with higher number of data in the training file.

2.

Table 2 lists a group of solutions containing a constant sulfide concentration of 0.5 M, and different combinations of EA and carbonate concentrations. The variation of the EA and carbonate concentration represents the variations of these concentrations found from the start of a causticizing process to its end. Also listed in the table are the values predicted. The agreement is very good.

3.

Figure 11 shows the spectra of a group of kraft white and green liquors. The spectra were obtained with a one-reflectance ATR prism, which were then used to built another calibration file. This new calibration file is to analyze a set of kraft liquors obtained from a kraft pulp mill. The measured concentrations of NaOH, Na₂CO₃ and Na₂S by ABC titration, and predicted by present method are listed in Table 3. Sample GL is a green liquor, while samples, WL-1, WL-2 and WL-3, are white liquors from different units of the causticizing plant. The agreement of the values from ABC titration and present method is very good

Na₂S concentration. For NaOH and Na₂CO₃, the errors are quite acceptable for mill process control purpose.

CONCLUSION (BASES FOR CLAIMS)

1. This method based on the ATR-UV technology can simultaneously determine sodium hydroxide, sulfide and carbonate concentrations in kraft liquor used in kraft pulp manufacturing process.
2. This method is very rapid. In an industrial and computer-automated setup, a determination can be achieved in 2-5 seconds. This is basically the data sampling rate, which can be fed to the control loops of each specific operation.
3. This method is very simple, and requires no manual liquor sampling when the initial calibration file is built.
4. This method does not need frequent maintenance.
5. This method can be used as an on-line sensor device or as an in-line sensor device.
6. This method can be used to control the sulfate reduction efficiency in chemical recovery furnace.
7. This method can be used to control the causticizing efficiency in recausticization plant.
8. This method can be used to control the pulping quality and cooking chemical consumption by more accurate controlling cooking chemical charges, i.e. white liquor, to the digester.
9. This method can be used to control the white liquor oxidation reactor by accurate measurement of the sulfide and thiothsulfate concentrations.

Reference

1. J.N. Harrick, *Internal Reflection Spectroscopy*, Wiley, New York, 1967.
2. H. Schlemmer and J. Katzer, *ATR technique for UV/VIS analytical measurements*, *Fresenius Zeitschrift für Analytische Chemie*, 329, 435-439 (1987).
3. Xin-Sheng Chai *Process Analytical Chemistry Applied to Liquors in the Pulping Industry*, Doctoral Thesis, ISBN 91-7170-653-4 (1996).
4. L-G Danielsson and Chai Xin Sheng, *Spectroscopic measurements in opaque solutions. UV-VIS spectroscopy on process liquors in the paper and pulp industries*. *Process Control and Quality*, 6 (1994) 149-157.
5. Xin-Sheng Chai, L-G Danielsson, Xiaotian Yang and Mårten Behm, *Spectrophotometric in-line process monitoring in UV-Vis range using an ATR-probe*, *Process Control and Quality*, In press, 1998.

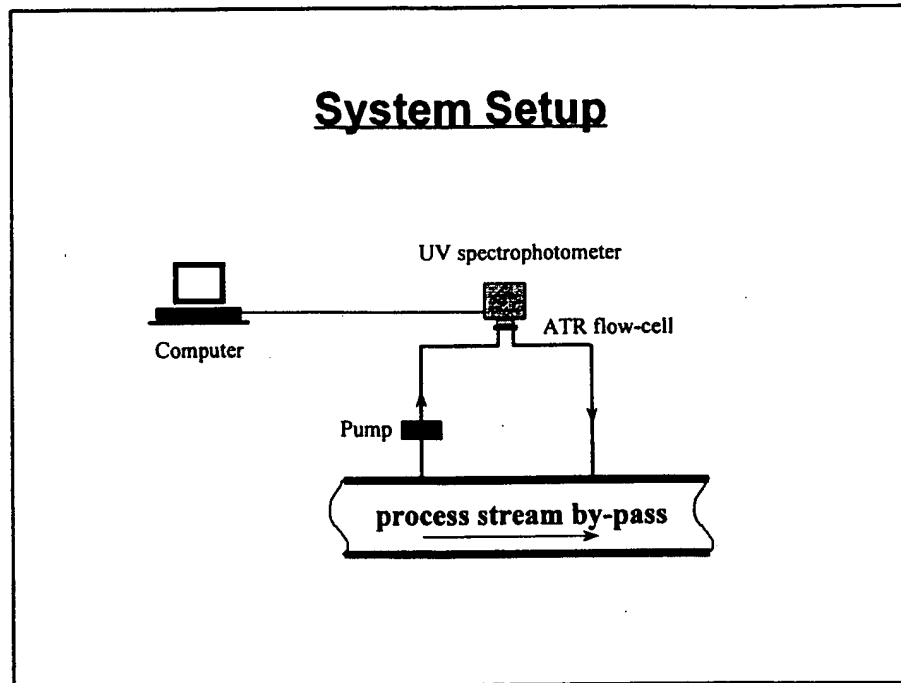


Figure 1

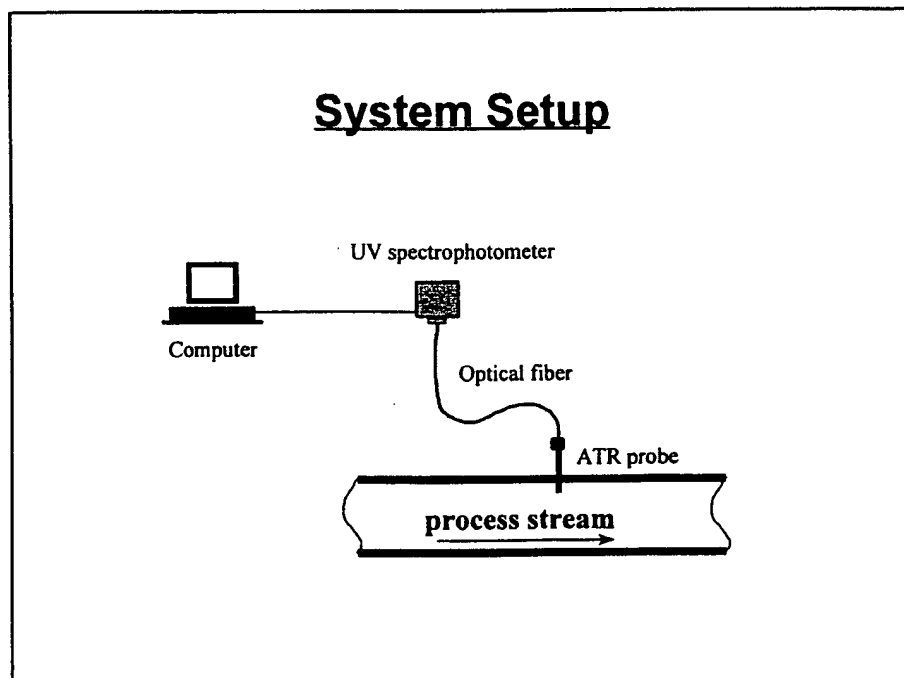


Figure 2.

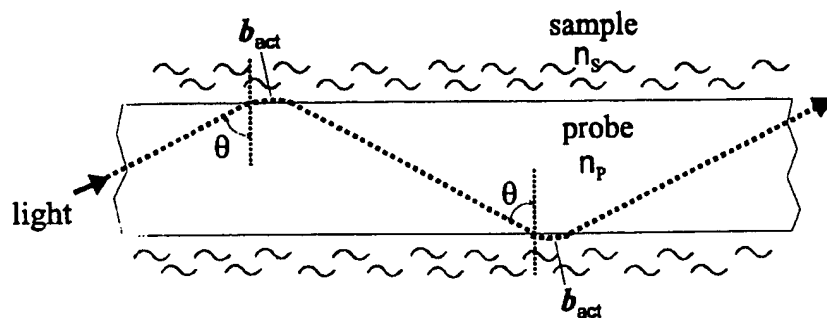


Figure 3. Principle of ATR

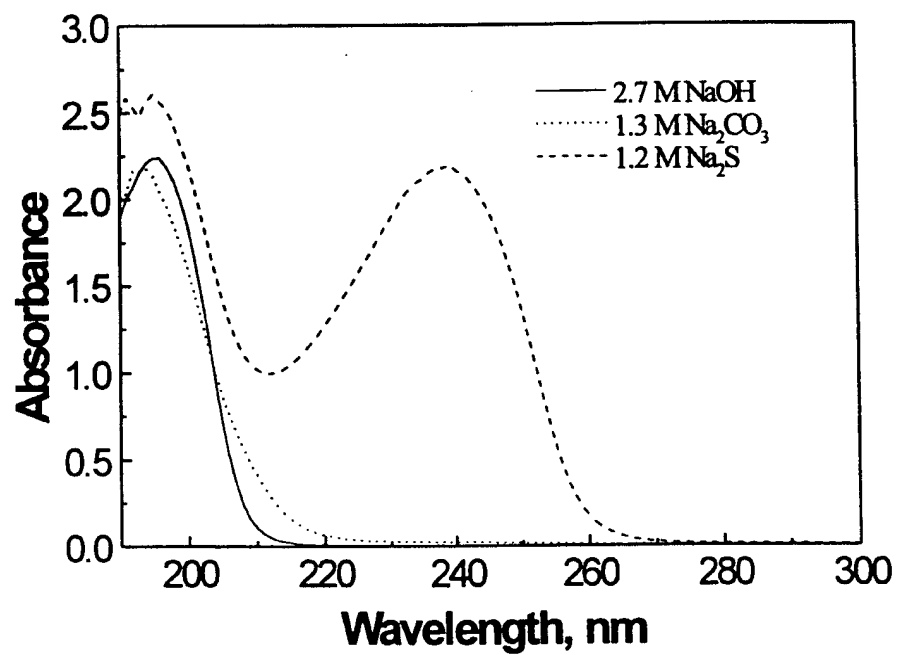


Figure 4.

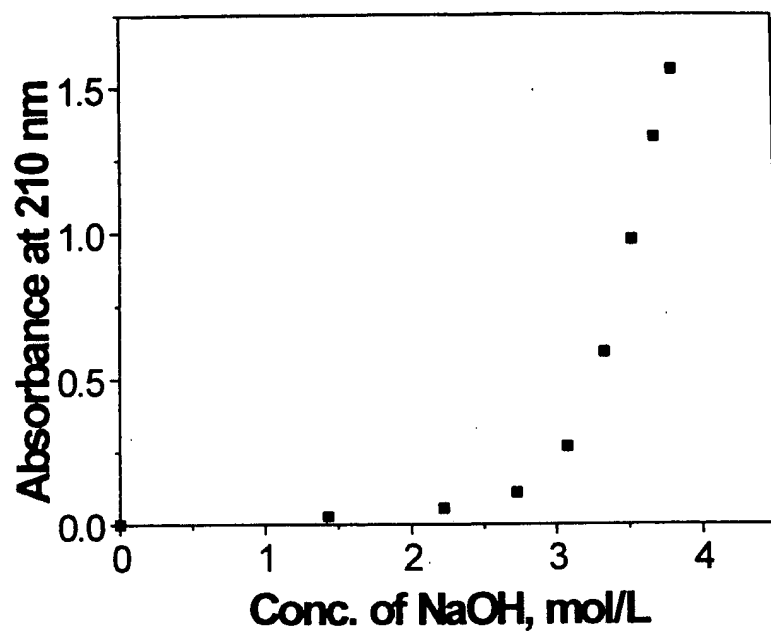


Figure 5.

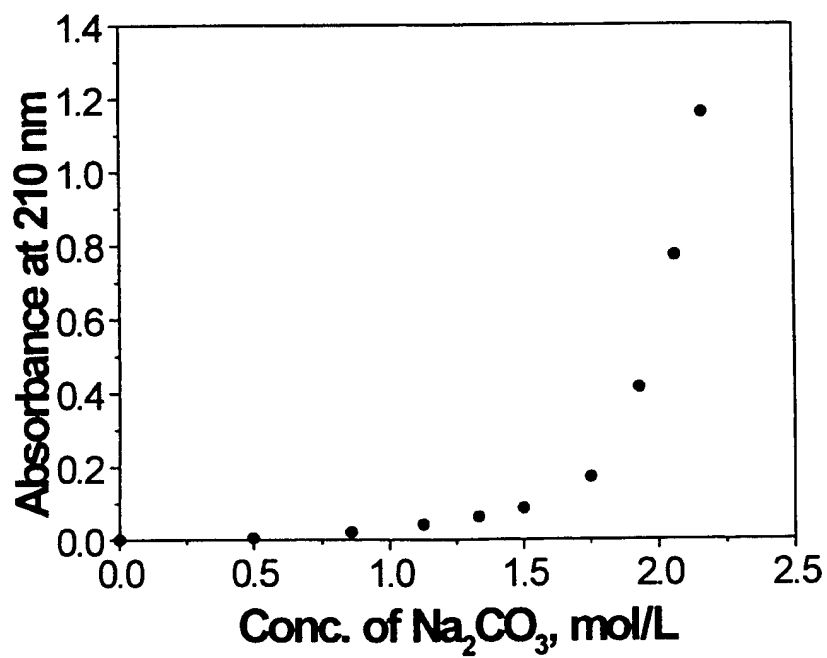


Figure 6.

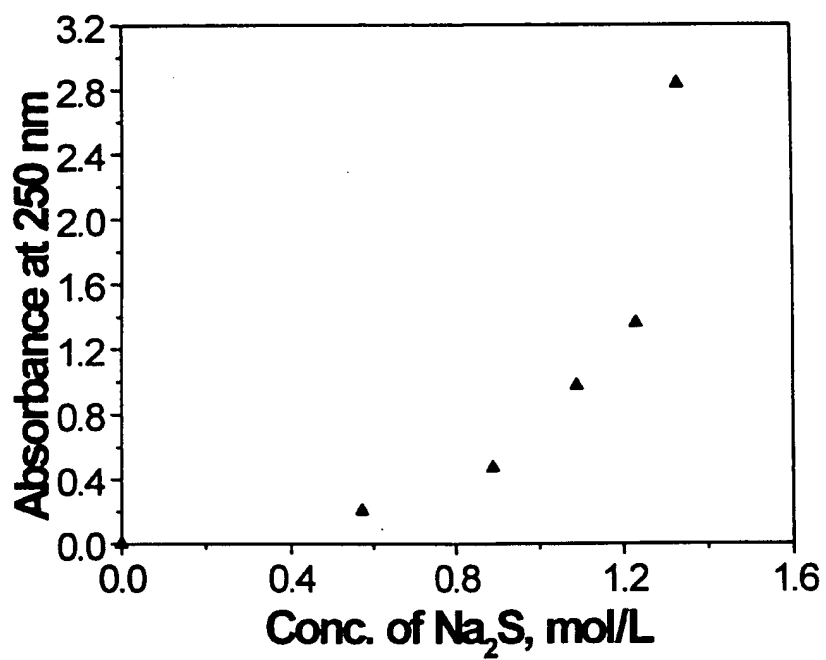


Figure 7.

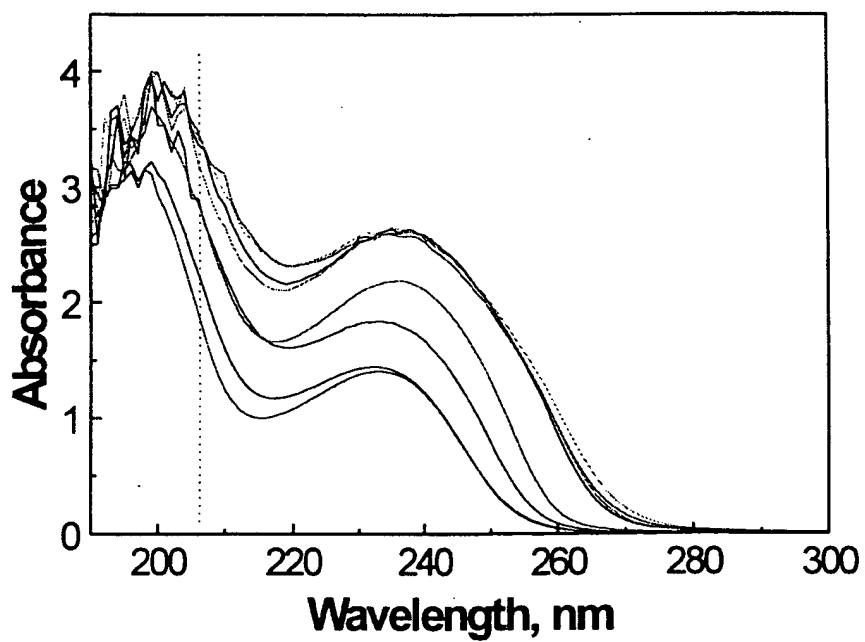


Figure 8.

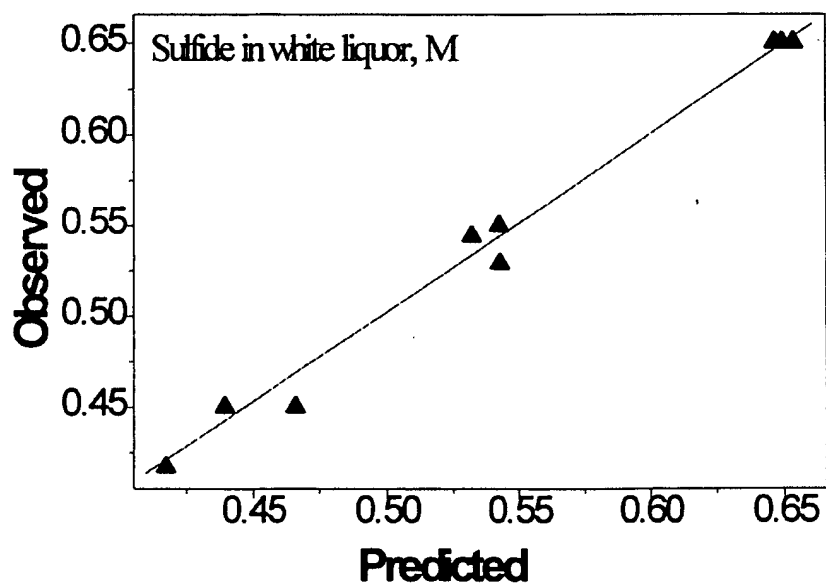
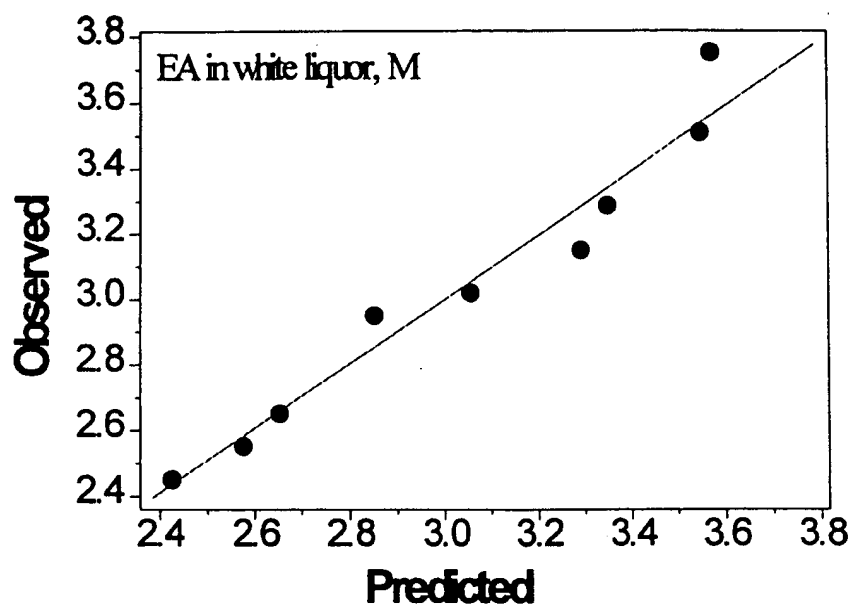


Figure 9.

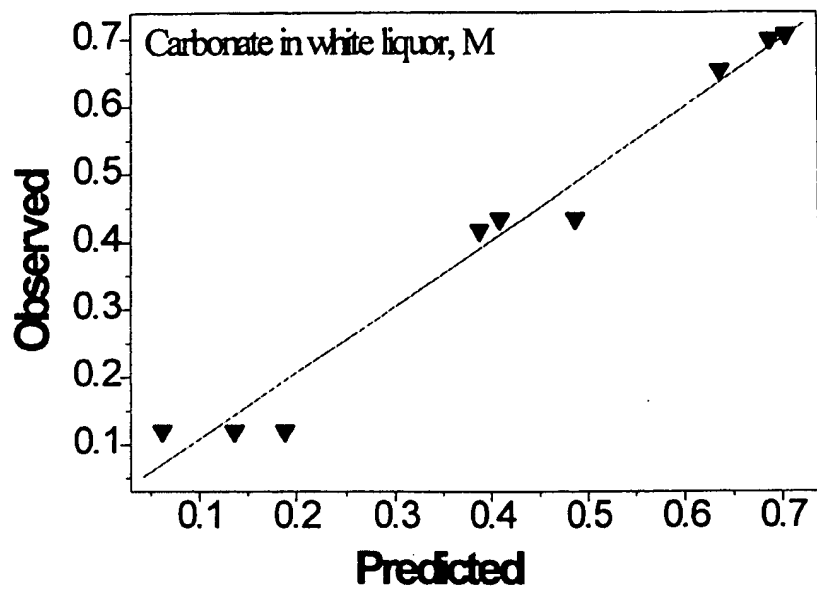


Figure 10.

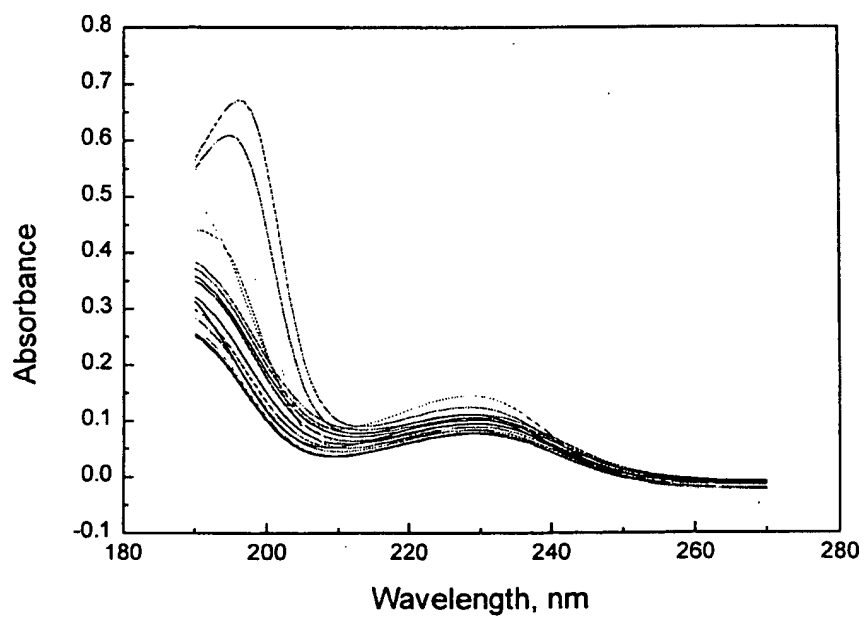


Figure 11.

Table 1. Comparison between actual (Obs.) and predicted (by model) data.

Sample	Effective Alkali, M			Sulfide, M			Carbonate, M		
	Obs.	Pred.	Err., %	Obs.	Pred.	Err. %	Obs.	Pred.	Err. %
1	2.45	2.42	-1.22	0.45	0.47	4.44	0.44	0.41	-6.82
2	2.55	2.58	1.17	0.55	0.54	-1.82	0.12	0.14	16.7
3	2.65	2.65	0	0.65	0.65	0	0.70	0.71	1.43
4	2.95	2.85	-3.39	0.45	0.44	-2.22	0.44	0.49	11.4
5	3.02	3.06	1.32	0.54	0.53	-1.85	0.70	0.69	-1.43
6	3.15	3.29	4.44	0.65	0.65	0	0.12	0.06	-50.0
7	3.29	3.35	1.82	0.42	0.42	0	0.65	0.64	-1.54
8	3.51	3.55	1.14	0.53	0.54	1.89	0.42	0.39	-7.14
9	3.75	3.57	-4.80	0.65	0.65	0	0.12	0.19	58.3

Table 2. Comparison between actual (Obs.) and predicted (by model) data.

Sample No.	Concentration of EA, M			Concentration of carbonate, M		
	Obs.	Pred.	RSD, %	Obs.	Pred.	RSD, %
1	0.971	0.980	0.93	1.748	1.743	-0.29
2	1.335	1.329	-0.45	1.558	1.561	0.19
3*	1.699	1.738	2.29	1.369	1.349	-1.46
4	2.063	2.026	-1.79	1.180	1.199	1.61
5	2.427	2.468	1.69	0.990	0.969	-2.12
6	2.791	2.781	-0.36	0.801	0.806	0.62
7*	3.155	3.222	2.12	0.612	0.577	-5.72
8	3.519	3.564	1.28	0.422	0.399	-5.45
9	3.883	3.843	-1.03	0.233	0.254	9.01

Table 3. Chemical concentrations of mill liquors measured by ABC titration and predicted by the present method

Sample type*	NaOH, g/L			Na ₂ S, g/L			Na ₂ CO ₃		
	ABC	Pred.	RSD, %	ABC	Pred.	RSD, %	ABC	Pred.	RSD, %
GL	47.2	48.9	3.8	33.9	34.3	1.3	54.4	51.9	-4.7
WL-1	107.6	109.3	1.5	29.1	29.2	0.4	36.0	33.4	-7.2
WL-2	110.9	113.4	2.2	29.5	29.4	-0.1	30.8	29.9	-2.8
WL-3	97.9	95.6	-2.4	30.8	30.6	-0.6	35.3	38.6	9.3